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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : B41M 5/00, D06P 5/00, D04H 3/16	A1	(11) International Publication Number:	WO 99/33669
		(43) International Publication Date:	8 July 1999 (08.07.99)

(21) International Application Number: PCT/US98/27342

(22) International Filing Date: 21 December 1998 (21.12.98)

(30) Priority Data:

60/070,038	30 December 1997 (30.12.97)	US
60/076,066	26 February 1998 (26.02.98)	US
09/140,081	25 August 1998 (25.08.98)	US

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(81) Designated States: CA, CN, JP, KR, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: FIBROUS INK–JET PRINTING MEDIA

(57) Abstract

A media for ink jet printing is provided that improves the water fastness of the inks on the media, improves the absorption of aqueous inks into the media, and makes ink jet printed images on the media appear chromatic and clear. An ink/media set is also provided. The printing media is a fibrous fabric or sheet substrate that has been treated with a positively charged species to make pigments in such jetted inks strongly bind to the fibers of the media. Where appropriate, the printing media also includes a wetting agent to make the media readily absorb jetted inks. The media has high tensile and tear strengths making it suitable for outdoor signs and banners.

wetting agent = surfactants

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TITLE

FIBROUS INK-JET PRINTING MEDIA

FIELD OF THE INVENTION

This invention relates to printing media, and more particularly, to a fibrous sheet material that has been treated to enhance the quality of images printed on the sheet material with an ink jet printer.

BACKGROUND OF THE INVENTION

Ink jet printing is a non-impact method for recording information in response to an electronic signal, such as that generated by a computer. In an ink jet printer, an electronic signal generates droplets of ink that are deposited on a printing media such as a paper or film sheet. Ink jet printers have found broad commercial acceptance due to their reliability, relatively quiet operation, graphic capability, print quality, and low cost.

In current ink jet printers, several primary inks (typically black, cyan, magenta and yellow) are used to print textual and graphic information on a printing media. These inks are composed primarily of water, and contain a colorant that may be a dye or pigment dispersion. Dye-based inks tend to fade when exposed to sunlight. Pigment-based inks offer better light stability, especially when used in outdoor applications. Most ink jet printing inks also contain a polyhydric alcohol to prevent nozzle clogging, and they may contain various other minor additives as well. U.S. Patent No. 5,085,698 (assigned to E.I. du Pont de Nemours & Company (hereinafter "DuPont")) discloses pigmented inks suitable for use in ink jet printing.

An ink jet printed image consists of discrete dots of ink. In order to print colored pictorial information, such as photographs or complex graphics, it is important that the dots have well defined boundaries. Bleeding or wicking of the ink on the printing media reduces the resolution of the image. An ink jet printed image will also degrade if the image smears easily after application, as occurs when a printed image is physically contacted before the ink is fully dried. Printed colors are obtained by combining primary inks at ink loadings that often exceed that required for 100% coverage. Where inks are applied in such a high density fashion, it is very important that the ink be absorbed into the media quickly such that the inks dry before having an opportunity to smear.

Ink jet printing is frequently done on ordinary paper. Paper is a suitable media for many desk-top publishing applications where the sheet is not to be subjected to adverse physical conditions such as wind, rain and sunlight. In applications where the printing media must be durable under adverse physical conditions over extended periods of time, such as where printed sheets are used in maps, packaging materials, or outdoor signs and banners, a printing media that is stronger and more durable than paper is needed. Printing media used in outdoor applications or under other adverse physical conditions must be of high strength, and it must be capable of both receiving and retaining a high resolution image, even after prolonged exposure to wind, rain and sunlight. An ink jet printable media suitable for use under adverse physical conditions, such as outdoor applications, must not wrinkle or otherwise distort when wetted. The strength of the media must also be maintained over extended periods of time, without regard to exposure to wind, rain and sunlight. On the other hand, the ink jet printable media must rapidly absorb the water present in ink jet printing inks, even when the ink is printed at a high density and at a high speed, in order to keep the ink from flooding the media's surface. At the same time, an ink jet printable media must not promote the wicking of ink over the surface of the media or the printed image will become more fuzzy and transparent than is desirable.

Synthetic fibrous sheets, such as sheets made of spunbonded polyolefins, are strong, durable and flexible. However, when conventional ink jet printing inks are jetted directly onto synthetic fibrous sheets, the printed image is very poor. The color is washed out and the image definition is poor (*i.e.*, undefined boundaries between colors as well as wicking of color into unprinted areas). Accordingly, ink jet printing media currently used for printed products that must withstand adverse physical conditions are made of two or more layers. Such materials generally include a support layer made of a high strength sheet material, such as vinyl or nylon, and an ink receptive layer of one or more printable hydrophilic layers coated on the support layer. PCT Publication No. WO 97/01448 discloses an ink jet printing substrate comprised of a film or nonwoven web coated with a second layer that includes a latex binder, hydrophilic silica, a cationic polymer, and a surfactant. U.S. Patent No. 4,775,594 discloses an ink jet printable transparency material comprised of a polyester film coated with a clear coating that includes a clear polymer resin and non-volatile organic acid. U.S. Patent 5,429,860 (assigned to DuPont) discloses an ink jet printable sheet comprised of a support sheet coated with a hydrophilic polymer binder that includes a reactive component, such as acid or base groups, that help bind the ink to the sheet material.

Coated printing sheets are bulkier and more expensive to produce than is desirable. What is needed is a less bulky and less expensive single layer sheet material that is strong and durable yet is also ink jet printable. The single layer sheet material must also readily absorb water-based ink jet printing inks, even when the inks are rapidly applied at high printing densities. If such an ink jet printable sheet material is to be suitable for outdoor applications, the single layer sheet material must also retain ink jet printed inks even after the printed sheets are exposed to wind, rain and sunlight.

SUMMARY OF THE INVENTION

The present invention provides an ink jet printable media comprising a fibrous polymeric substrate having positively charged species on the surface thereof. The ink jet printable media of the invention is a unitary sheet structure having a tensile strength of at least 20 N/2.54 cm, a basis weight of less than 8 oz/yd^2, a water absorption rate, according to TAPPI T558 pm-95, of at least 0.01 microl/mm^2/sec, and a color washout, according to the IJE method, of less than 50%. Preferably, the fibrous polymeric substrate is a nonwoven sheet such as a spunbonded polyolefin sheet. The fibrous substrate may be comprised of fibers having positively charged colloidal silica and a wetting agent on the surface of the fibers. Alternatively, the fibrous substrate may be comprised of fibers having positively charged protons, metal ions, or cationic polymers on the surface of the fibers and, where necessary, a wetting agent on the surface of the fibers.

The present invention also provides an ink/printing media set comprising: (a) an ink comprising an insoluble colorant in an aqueous carrier medium; and (b) an ink jet printable media like that described in the preceding paragraph. The present invention also provides a process for making an ink jet printable media comprising the steps of: (1) forming a solution comprising water, and a source of positively charged species; (2) wetting a fibrous polymeric substrate with the solution, the substrate having a tensile strength of at least 20 N/2.54 cm and a basis weight of less than 8 oz/yd^2; and (3) drying the substrate such that the dried substrate has a water absorption rate, according to TAPPI T558 pm-95, of at least 0.01 microl/mm^2/sec, and a color washout, according to IJE method, of less than 50%. The source of positively charged species is preferably selected from the group of positively charged colloids, acids, cationic polymeric materials, and water soluble compounds of calcium, aluminum, magnesium and zirconium. The process may include the additional step of adding a wetting agent to the solution before wetting the fibrous substrate with the solution if the fibers of the substrate are not easily wettable. The printing media treated according to the

process of the invention has a four color optical density, measured according to the OD method, that is at least 8% greater than the four color optical density of the fibrous polymeric substrate before the substrate is wetted with the treatment solution.

A more thorough explanation of the invention will be provided in the detailed description of the preferred embodiments that follows.

DETAILED DESCRIPTION

The present invention provides a media for ink jet printing that improves the water fastness of the inks on the media and improves the absorption of aqueous inks into the media. The invention also provides both a media on which ink jet printed images appear chromatic (because colorants are kept near the surface of the media) and a media on which images can be printed in a manner such that the lines and edges of the images are well defined and clear. The printing media of the invention is a fibrous fabric or sheet substrate that has been treated both to make the media readily absorb jetted inks and to make pigments and dyes in such jetted inks strongly bind to the fibers of the media. Preferably, the media has high tensile and tear strengths so as to give the media utility in outdoor applications such as signs and banners.

The invention also provides an ink and printing media set. The ink of this ink/media set is a dye-based or pigment-based aqueous ink jet printing ink. The preferred pigmented inks maintain their color even after prolonged exposure to sunlight. Dye-based and pigment-based inks are described in U.S. Patent No. 5,429,860 (assigned to DuPont), which is hereby incorporated by reference. The preparation of the more preferred pigment-based inks is described in the examples below. The printing media of the ink/media set is the printing media disclosed in this patent application.

The ink jet printing media of the invention is comprised of a fibrous substrate that has been treated to make the substrate significantly more ink jet printable. The fibrous substrate is preferably a woven or nonwoven sheet or fabric. It is further preferred that the fibers of the fibrous substrate polymeric fibers. As used herein, "fibrous polymeric substrate" refers to fabrics and sheets, both woven and nonwoven, made in substantial part of synthetic polymers fibers such as polyamide fibers, polyester fibers, or polyolefin fibers; of blends of such synthetic fibers; or of blends of natural and synthetic fibers. It is further preferred that the printing media be a unitary structure. As used herein, the term "unitary structure" is used to designate woven or nonwoven fabrics or sheets made of the same types of fibers or fiber blends throughout the thickness of the fabric or sheet

structure, wherein the fibers form a substantially homogeneous layer that is free of distinguishable coated layers or laminations.

According to the preferred embodiments of the invention, the fibrous substrate of the ink jet printing media is a unitary structure made of a nonwoven sheet or woven fabric, which sheet or fabric is strong, tear resistant and does not rapidly degrade when exposed to the weather and to sunlight. A preferred fibrous substrate is a fibrous polyolefin sheet. Suitable polyolefin fibrous sheet materials include polypropylene and polyethylene spunbonded webs, scrims, woven slit films, carded webs, flash-spun webs, and woven or nonwoven sheets comprised of blends of polyolefin fibers or of polyolefin fibers and other fibers. Preferred woven fabrics for the fibrous substrate include fabrics made in substantial part from polyamide, polyester and polyolefin fibers. Preferred woven fabrics for the printing media include fabrics made from nylon 6,6, DACRON® polyester, and blends of polyester and natural fibers such as cotton. DACRON® is a registered trademark of DuPont.

Nonwoven sheets made from flash-spun polyethylene plexifilamentary fiber webs, as disclosed in U.S. Patent Nos. 3,169,899 and 3,532,589 (both assigned to DuPont), which are hereby incorporated by reference, are an especially preferred fibrous substrate material for use in the ink jet printable media of the invention. The term "plexifilamentary" means a three-dimensional integral network of a multitude of thin, ribbon-like, film-fibril elements of random length and with a mean film thickness of less than about 4 microns and with a median fibril width of less than about 25 microns. In plexifilamentary structures, the film-fibril elements are generally coextensively aligned with the longitudinal axis of the structure and they intermittently unite and separate at irregular intervals in various places throughout the length, width and thickness of the structure to form a continuous three-dimensional network.

One such plexifilamentary sheet material is TYVEK® spunbonded olefin sheet material sold by DuPont. TYVEK® is a registered trademark of DuPont. TYVEK® sheets are made from flash-spun polyethylene that has been thermally bonded to form lightweight sheets that have outstanding strength while also exhibiting good tolerance to ordinary weather conditions. In addition, because TYVEK® sheet material is made from high density polyethylene, it is readily recyclable. TYVEK® sheet material can be made with stabilizers added to the polyethylene that make the sheets more resistant to degradation resulting from prolonged exposure to heat or UV radiation. Antioxidants (such as Irganox 1010 also made by Ciba-Geigy) and acid neutralizers (such as calcium stearate) can also be added to the polymer fibers of the sheet in order to reduce degradation during

extended weathering. Hydroxylamine stabilizers may also be added to the fibers of the sheet in order to stabilize TYVEK® sheets against UV degradation.

Particularly well suited for the fibrous substrate of the ink jet printable media of the invention is TYVEK® Type 1082C sheet material, due to its high tensile and tear strength. TYVEK® 1082C sheet material has a thickness of about 255 microns and a basis weight of about 101 g/m^2 (3.0 oz/yd^2). TYVEK® 1082C sheet material has an Elmendorf tear strength of between 5.0 and 9.2 Newtons and a tensile strength of about 360 N/2.54 cm.

According to the invention, the fibrous substrate is treated with a positively charged species that serves to bind the color pigments or dyes in ink jet printing inks to the fibers of the fibrous substrate. Where the fibrous substrate is comprised of hydrophobic fibers, as is the case with most synthetic polymer fabrics and sheets, it is also preferred that the fibrous substrate be treated with a wetting agent. Preferably, the positively charged species and the wetting agent are applied to the fibrous substrate in the form of a liquid mixture or solution. The wetting agent makes it possible for a liquid treatment mixture or solution to thoroughly contact the fibrous substrate such that positively charged species in the treatment mixture or solution reach as many of the fibers of the fibrous substrate as is possible. Henceforth, the term "treatment solution" is defined to include both true solutions and colloidal dispersions.

The fibrous substrate may be treated with a treatment solution containing positively charged species, and a wetting agent where appropriate, by dipping the fibrous substrate in the treatment solution and then drying the substrate. Preferably, the fibrous substrate is dipped in the treatment solution long enough to saturate the substrate. When the substrate is removed from the treatment solution, excess solution is squeezed out of the substrate after which the substrate is air or oven dried. Alternatively, the treatment solution may be applied to the fibrous substrate with an applicator roll, a spray applicator, an air knife, or a Meyer rod. Even after the treatment solution has dried on the fibrous substrate, the positively charged species and wetting agent remain on the fibers of the substrate. The wetting agent renders the fibers more hydrophilic (*i.e.*, more receptive to aqueous ink jet printing inks). As used herein, "aqueous printing inks" are defined as water-based inks that may include other liquids such as alcohols. It is believed that the positively charged species form protonated sites on the substrate fibers that serve to trap the pigment or dye of an aqueous ink in fibers near the surface of the fibrous substrate.

The preferred ink jet printing inks are pigmented inks because pigmented inks retain color better than other inks, especially in outdoor

applications. Pigmented ink jet printing inks are dispersions of pigment in an aqueous carrier medium that are prepared as described in the examples below. The pigment in pigmented ink jet printing inks is normally anionic, but may also be cationic. Where the pigment is cationic, the positively charged species of the printing media would preferably be replaced with a negatively charged species.

The stability of a pigmented ink dispersion depends on the ability of the dispersant to remain dissolved or dispersed in the carrier medium. Destabilization of a pigment dispersion occurs when the dispersant is rendered less-dispersed, less-soluble or non-soluble in the carrier medium. This results in the precipitation of the pigment dispersion. This precipitation is also commonly known as flocculation or coagulation. Without wishing to be bound by theory, it is believed that the positively charged species on the surface of the treated fibrous printing media of the invention serve to: (1) destabilize the pigment dispersion so as to cause flocculation of the charged pigment; (2) attract the oppositely charged pigments in the ink to the fibers of the substrate; and (3) trap the pigments near the surface of the substrate as the aqueous portion of the ink is rapidly absorbed into the fibrous substrate. If the printing media of the invention is used with dye-based ink jet printing inks, it is believed that the positively charged species of the printing media of the invention will insolubilize the dyestuff which causes precipitation of dyes onto the fibrous substrate. This precipitation is commonly referred to as dye fixation.

Sources of positively charged species that have been found to make a fibrous substrate more ink jet printable include positively charged colloids, strong acids, aluminum chlorohydrate, aluminum zirconium tetrachlorohydrex glycine, calcium chloride, and combinations thereof. Cationic coagulating and flocculating agents such as calcium, aluminum, magnesium, and zirconium metal ions and polymeric materials with positively charged sites (*e.g.*, amine and amide sites) can also serve as a source of the positively charged species. The positively charged species are applied to the fibers of the fibrous substrate by way of a treatment solution.

The addition of wetting agents to the treatment solution have been found to make a fibrous substrate more ink jet printable. Such wetting agents include ionic, amphoteric, and nonionic surfactants. Wetting agents in the treatment solution help insure that the treatment solution penetrates and treats hard to reach fibers of the printing media substrate. Other minor ingredients may be added to the treatment solution to improve mixing and application of the solution to the printing media substrate. For example, known defoamers may be added to the treatment solution in order to reduce foaming during application of the

solution to the printing media substrate. Miscible solvents, such as isopropyl alcohol, may also be added to the treatment solution in minor amounts so as to improve the compatibility of the ingredients in the solution and to make the solution more stable.

The concentration of active ingredients in the treatment solution will depend on the desired level of image brightness and vividness (measured in terms of optical density), the desired resistance to color washout, and the desired rub resistance for the ink jet printed matter on the printing media. The actual concentration of the active ingredients on the printing media depends on the wet pick-up during treatment of the media with the treatment solution as well as on the concentration of the active ingredients in the treatment solution. Higher concentrations of active ingredients on the printing media can also be achieved by way of multiple treatments with the treatment solutions. Where the treatment solution is applied by means of a spray, roll, air knife or Meyer rod applicator, it is anticipated that the treatment solution may be applied more than one time to the same surface of the printing media to make the treatment more uniform. It is also anticipated that the treatment solution may be applied to both sides of a printing media substrate, especially where a user of the printing media might want to print on both sides of the printing media.

According to one preferred embodiment of the invention, the treatment solution for treating a fibrous polymeric substrate to make the substrate more ink jet printable includes calcium chloride, positively charged colloidal silica and one or more surfactants (*See* Examples 4-8). One positively charged colloidal silica that has been found to dramatically improve the ink jet printability of a polyolefin-based substrate is LUDOX® CL-P positively charged colloidal silica (40% solids) sold by DuPont. LUDOX® is a registered trademark of DuPont. Colloidal silica has been found to be especially effective for treating a fibrous substrate to make an ink jet printable medium when the treatment solution also includes calcium chloride as an additional source of positively charged ions. Two surfactants that have been combined with colloidal silica and calcium chloride in the treatment solution are alcohol ethoxylate propoxylate (MERPOL® LF-H sold by DuPont), and polyalkyleneoxide modified heptamethyltrisiloxane (SILWET® L-77 sold by WITCO Corporation of Greenwich, Connecticut).

According to another embodiment of the invention, the solution for treating a fibrous polymeric substrate to make a more ink jet printable media may be comprised of an acid, used either alone or in combination with a surfactant. One acid that has been found to be especially effective at improving the ink jet

printability of a fibrous substrate is phosphoric acid, especially when used in combination with citric acid and a surfactant (*See* Examples 10-16).

According to another preferred embodiment of the invention, the treatment solution for treating a fibrous polymeric substrate to make the substrate more ink jet printable may comprise calcium chloride, positively charged colloidal silica, aluminum chlorohydrate, aluminum zirconium tetrachlorohydrex glycine, and one or more surfactants in water (*See* Examples 17-20). A preferred surfactant is the nonionic alcohol ethoxylate surfactant TERGITOL® TMN-6 sold by Union Carbide Corporation of Danbury, Connecticut. Other non-acid sources of positively charged species for the printing media include n-butyl phosphate ester (Example 21) and polymeric complexing agents (Examples 22 and 23).

As can be seen in Examples 38-62, treatment of a variety of fibrous substrates with various acids, even without a surfactant being present in the treatment solution, improves the optical density of an ink jet printed image. Where the acid had a pH of less than 2.2, the use of an acid alone improved the optical density of an ink jet printed image on a treated fibrous substrate. Treatment with such a solution also reduced the bleed observed in images printed on acid-treated substrates. The effectiveness of the acids used in Examples 38-62 with regard to reducing image bleed and improving optical density ("OD") is summarized below:

PROPERTIES (in water, 20°C)

ACID (concentration)	solubility	pK_1	pH	Effectiveness
benzoic acid (~0.3%)	~ 0.3%	4.20	2.90	not significant for either bleed or OD
caprylic acid (~0.1%)	~0.1%	4.89	3.74	not significant for either bleed or OD
valeric acid (~3%)	~3%	4.84	2.69	not significant for bleed; yes for OD
tetra-boric acid (~5%)	~5.5%	4.00	2.25	not significant for bleed; yes for OD
sulfanilic acid (~2%)	~2%	3.22	2.09	yes for bleed & OD
succinic acid (10%)	> 8%	4.21	2.14	yes for bleed & OD
methoxyacetic acid (20%)	freely sol.	3.57	1.61	yes for bleed & OD
malic acid (20%)	~56%	3.46	1.64	yes for bleed & OD
citric acid (20%)	~60%	3.13	1.56	yes for bleed & OD
phosphoric acid (20%)	freely sol.	2.15	0.91	yes for bleed & OD
maleic acid (20%)	freely sol.	1.91	0.84	yes for bleed & OD
oxalic acid (14%)	~14%	1.27	0.54	yes for bleed & OD
sulfamic acid (10%)	~15%	0.99	0.04	yes for bleed & OD
hydrochloric acid (3%)	freely sol.	-6.1	0.04	yes for bleed & OD

Sulfuric acid and various inorganic acids have also been found to improve the ink jet printability of a fibrous substrate. One drawback to acid treatments is that the acids may degrade the substrate or react with things contacting the treated substrate. For this reason the printing media of Examples 4-7 and 17-20 are the more preferred embodiments of the invention.

When a fibrous substrate is treated as described above, a printing media is produced on which ink jet printed images are sharper and more chromatic. Images on the printing media of the invention exhibit low color washout upon wetting as well as very good wet and dry rub resistance. It is anticipated that wet and dry rub resistance can be further improved by the application of commercially available water-based or solvent-based coatings over

the printed image. Such coatings include RHOPLEX® Emulsion E-2321 from Rohm & Haas of Philadelphia, Pennsylvania and WATER-MAT available from Water-Mat, Inc. of Syracuse, New York.

The printing media of the invention is an economic ink jet printable media with a unitary structure that retains ink jet printed inks and has the strength and durability needed for rigorous applications. As exemplified below, the ink jet printing media of the invention can be attached to other substrates, such as solid surfaces, fabrics or reinforcing scrim materials.

The following non-limiting examples are intended to illustrate the product and process of the invention and not to limit the invention in any manner.

EXAMPLES

In the examples below, samples of sheet material were saturated with various treatment solutions and then passed between rubber-coated nip rollers to squeeze out excess treatment solution. The samples were then oven dried. As described in the examples below, the dried samples were tested for one or more of the following properties: water absorption; ink jet printed color washout; readability of an ink jet printed bar code; and optical density of the ink jet printed color.

Preparation of Inks

Preparation of Dispersant 1

A 1-liter flask was equipped with a mechanical stirrer, thermometer, nitrogen inlet, drying tube outlet, and addition funnels. Tetrahydrofuran (THF), 164g, tetrabutyl ammonium m-chlorobenzoate (TBACB), 0.5g, and 1,1-bis(trimethylsiloxy)-2-methyl propene, 15g, were charged to the flask. Feed 1 (THF, 20g; TBACB, 0.5g) was started and added over 120min. Feed 2 (trimethylsilyl methacrylic acid, 102g) was started at the same time and added over 30 minutes. Thirty minutes after the addition of Feed 2, Feed 3 (n-butyl methacrylate, 92g; methyl methacrylate, 32g) was started and added over the next 30 minutes. An hour after Feed 3 was completed, 50 g of methanol were added and 100g of volatiles were removed by distillation.

Preparation of Dispersant 2

A 1-liter flask was equipped with a mechanical stirrer, thermometer, nitrogen inlet, drying tube outlet, and addition funnels. THF, 194g, and TBACB, 1.2g, and 1,1-bis(trimethylsiloxy)-2-methyl propene, 14g, were charged to the flask. Feed 1 (THF, 20g; TBACB, 1g) was started and added over 120 min. Feed

2 (trimethylsilyl methacrylic acid, 95g) was started at the same time and added over 30 minutes. Thirty minutes after the addition of Feed 2, Feed 3 (benzyl methacrylate,138g) was started and added over the next 30 minutes. An hour after Feed 3 was completed, 25 g of methanol were added and 75g of volatiles were removed by distillation.

Preparation of Black Concentrate

A black dispersion was prepared using the following procedure:

Ingredient	Amount (parts)
FW18, Carbon Black pigment (Degussa Corp., Allendale, NJ)	200
Dispersant Solution 1	200
Isopropanol	500

The above mixture was charged to a 2-roll mill and processed for 45 minutes. This made a pigment chip that contains 67% pigment and 33% polymer. The chip, 300g, was neutralized with 42g of 45% potassium hydroxide solution and diluted with 1658g deionized water to make a black concentrate, at 10% pigment solids.

Preparation of Cyan Concentrate

A cyan dispersion was prepared using the following procedure:

Ingredient	Amount (parts)
Endurophthal® Blue GP, BT-617, (Cookson Pigment Inc., Newark NJ)	150
Dispersant Solution 2	200
Isopropanol	400

The above mixture was charged to a 2-roll mill and processed for 45 minutes. This made a pigment chip that contains 60% pigment and 40% polymer. The chip, 250g, was neutralized with 38g of 45% potassium hydroxide solution and diluted with 1212g deionized water to make a cyan concentrate, at 10% pigment solids.

Preparation of Magenta Concentrate

A magenta dispersion was prepared using the following procedure:

Ingredient	Amount (parts)
Quinacridone R-122 pigment (Sun Chemical Corp., Cincinnati OH)	150
Dispersant Solution 2	200
Isopropanol	400

The above mixture was charged to a 2-roll mill and processed for 45 minutes. This made a pigment chip that contains 60% pigment and 40% polymer. The chip, 250g, was neutralized with 38g of 45% potassium hydroxide solution and diluted with 1212g deionized water to make a magenta concentrate, at 10% pigment solids.

Preparation of Yellow Concentrate

A yellow dispersion was prepared using the following procedure:

Ingredient	Amount (parts)
Diarylide Y128 pigment (Sun Chemical Corp., Cincinnati OH)	180
Dispersant Solution 2	300
Isopropanol	500

The above mixture was charged to a 2-roll mill and processed for 45 minutes. This made a pigment chip that contains 55% pigment and 45% polymer. The chip, 330g, was neutralized with 57g of 45% potassium hydroxide solution and diluted with 1413g deionized water to make a yellow concentrate, at 10% pigment solids.

Preparation of Primary Inks

The four primary inks, black, cyan, magenta and yellow, used in Examples 1-37 were prepared by mixing together the following ingredients:

Pigment Dispersions:	**Black(K)**	**Cyan(C)**	**Magenta(M)**	**Yellow(Y)**
Ingredients				
Black Concentrate (g)	35.0	-	-	-
Cyan Concentrate (g)	-	10.0	-	-
Magenta Concentrate (g)	-	-	20.0	-
Yellow Congentrate (g)	-	-	-	30.0
Liponics® EG-1 (g)	5.7	5.0	5.0	6.0
Diethylene Glycol (g)	5.7	4.5	4.5	6.0
Surfynol 440 (g)	0.2	-	-	0.2
Zonyl® FSO (g)	-	0.05	0.05	-
Deionized Water (g)	51.6	80.5	70.5	60.5

The four primary inks, black, cyan, magenta and yellow, used in Examples 38-62 were prepared by mixing together the following ingredients:

Pigment Dispersions:	**Black(K)**	**Cyan(C)**	**Magenta(M)**	**Yellow(Y)**
Ingredients				
Black Concentrate (g)	35.0	-	-	-
Cyan Concentrate (g)	-	10.0	-	-
Magenta Concentrate (g)	-	-	20.0	-
Yellow Congentrate (g)	-	-	-	30.0
Liponics® EG-1 (g)	5.7	5.0	5.0	6.0
Diethylene Glycol (g)	5.7	4.5	4.5	4.5
Neopentyl Alcohol (g)	1.0	-	-	-
2-Pyrrolidone (g)	1.0	-	-	-
Zonyl® FSO (g)	-	0.05	0.05	0.05
Deionized Water (g)	51.6	80.5	70.5	60.5

Liponics® EG-1 is a short chain polyethylene glycol sold by Lipo Chem. Co. of Paterson, New Jersey. Zonyl® FSO is a surfactant sold by DuPont. Surfynol 440 is a surfactant sold by Air Products, Inc. of Allentown, Pennsylvania.

Printing

In Examples 1-37, the ink jet printing of inks used in the color washout and the optical density measurements was done with an Encad Novajet Pro-50 color ink jet printer, made by Encad, Inc. of San Diego, California. This Encad printer printed in color at 300 dpi x 300 dpi over its 50 inch printing width. The print pattern was a series of seven 0.5 inch by 0.5 inch squares of the following colors - black, cyan, yellow, magenta, red, green and blue. Optical density was measured on the color squares using an X-Rite® Densitometer, Model 418 (X-Rite Inc., Grandville, Michigan).

In Examples 1-25, the ink jet printing of black bar codes for bar code readability testing was done with a Hewlett Packard DeskJet 560c printer (Hewlett Packard, Palo Alto, CA) that printed at 300 x 300 dpi in color and 600 x 600 dpi in black.

In Examples 38-62, the Hewlett Packard DeskJet 560c ink jet printer was used for printing the series of seven 0.5 inch by 0.5 inch squares of the following colors - black, cyan, yellow, magenta, red, green and blue, used in measuring optical density. In Examples 38-62, optical density was measured on the color squares using an X-Rite® Densitometer, Model 418. The print pattern also included an array of colored lines on a yellow background to illustrate the control of ink spread and hence, the line acuity and resolution of the image.

Test Methods

In the description above and in the non-limiting examples that follow, the following test methods were employed to determine various reported characteristics and properties. ASTM refers to the American Society for Testing and Materials, TAPPI refers to the Technical Association of the Pulp and Paper Industry, and ANSI refers to the American National Standards Institute.

Basis Weight was determined by ASTM D-3776, which is hereby incorporated by reference, and is reported in g/m^2. The basis weights reported for the examples below are each based on an average of at least twelve measurements made on the sheet.

Absorption was measured using a video contact angle system, VCA 2500XE made by AST Products, Billerica, Massachusetts, following the TAPPI procedure T 558 pm-95. Three unprinted test specimens were cut from the sample to be tested, each 1 inch by 0.25 inches. A drop of deionized water was placed on each test piece in turn using as motorized syringe which was programmed to deposit a 0.8 microliter droplet. The syringe needle was removed from the water droplet by lowering the sample. The absorption of the water droplet into the test

specimens was recorded using a video camera programmed to record at a rate of either 14.5 frames per 3 seconds or 5 frames per 12 seconds, depending on the rate of absorption. The volume of the droplet in the first and last frames in which the droplet was evident was determined as was the difference between two droplet measurements. The droplet volume difference between the first and last frames in which the droplet was evident was divided by the time that elapsed between the first and last frames to determine the rate of absorption. The absorption rate was recorded in microliters per second per unit area of the specimen covered by the water droplet (microl/mm^2/sec).

Optical Density was measured according to a method developed by DuPont (referred to hereinafter as the "OD" method). The optical density is a measure of the amount of light reflected from a test sample. Optical density is the logarithm to the base 10 of the reciprocal of the amount of reflected light.

$$\text{Optical Density} = \log_{10} (1/\text{reflected light})$$

Optical Density was measured on a 0.5 inch by 4 inch sample strip printed as described above with a series of seven 0.5 inch by 0.5 inch printed squares of the following colors - black, cyan, yellow, magenta, red, green and blue. The black, cyan, yellow and magenta squares were printed with the primary inks described above. The red, green and blue squares were printed with combinations of the four primary inks.

The optical density of each color square was measured using an X-RITE Model 418 Densitometer (X-rite, Inc. Grandville, Michigan). The Densitometer was set up for status E density (ANSI/ISO 5-3-1995, ANSI/NAAPM IT2.18-1996). For each sample, the optical density of a section of an unprinted portion of the sample was measured. This measurement was stored in the Densitometer. The optical density was measured individually for each of the seven colors of the sample. The optical density recorded for each color was obtained by subtracting the optical density measured on the unprinted portion of the sample from the optical density measured on the printed portion.

The optical densities measured on the four primary colors (black, cyan, yellow, magenta) are reported for the examples below without dimensions. An average of the four primary color optical densities is reported as well. The percentage improvement in the optical density was determined using the average optical density calculated for each sample and the average optical density for an untreated control sample. The percent improvement in optical density was calculated as follows:

$$\text{Percent Improvement (optical density)} = \frac{\text{Avg. Optical Density (treated sample) - Avg. Optical Density (control)}}{\text{Avg. Optical Density (control)}} \times 100$$

Color Washout was measured according to the following method devised by DuPont's Ink Jet Enterprise, referred to hereinafter as the "IJE method". According to IJE method, washout was measured on a 0.5 inch by 4 inch sample strip that was printed with a series of seven 0.5 inch by 0.5 inch squares of the following colors - black, cyan, yellow, magenta, red, green and blue. The printing was performed according to the ink jet printing method described above using pigment-based inks, as described above. The optical density of each printed square was determined using an X-RITE Model 418 Densitometer as described above. The printed strip was then submerged in a beaker of water. A magnetic stir bar was then added and the beaker was placed on a standard lab magnetic stirrer. The stirrer was turned on and the sample was agitated for 30 minutes. The test sample was then removed from the beaker and air dried. The optical density of each of the seven colors was measured on the washed test sample using the X-RITE Model 418 Densitometer.

The percent of color washed out (a measure of the waterfastness) was determined from the optical densities measured on each of the seven colors before the sample was washed and after the sample was washed. The percent washout for each of the seven colors was averaged to obtain the overall color washout percent reported in the examples below. The percent color washout for each color was calculated as follows:

$$\text{Percent Washout (color)} = \frac{\text{Optical Density (pre-wash) - Optical Density (post-wash)}}{\text{Optical Density (pre-wash)}} \times 100$$

Bar Code Readability is measured according to ANSI X3.182-1990, which is hereby incorporated by reference. The ANSI X3.182-1990 test measures the print quality of a bar code for purposes of code readability. The test evaluates the print quality of a bar code symbol for contrast, modulation, defects, and decodability and assigns a grade of A, B, C, D or F for each category. An "A" grade is the highest grade and represents a highly readable code that can be decoded by the scanning unit with minimal mathematical computation. An "F" grade is the lowest grade for a bar code to which a scanner generates a response, and represents a bar code that requires extensive mathematical computation by the scanning unit to interpret. The overall grade of a sample is the lowest grade received in any of the above categories. A bar code is deemed "readable" if at least 7 of 10 scans of the bar code receive a grade of "F" or better.

The testing was done with Full ASCII Code 3-of-9 and UPC-A bar codes generated using Bar Tender for Windows software sold by Seagull Scientific Systems of Redmond, Washington. The bar codes were ink jet printed on the samples using the black inks described above with a Hewlett Packard DeskJet 560c printer that prints at 600 x 600 dpi (in black). The scanner was a PSC Quick Check 650 scanner with a 6 mil bandwidth, as manufactured by Photographic Sciences Corporation Inc. of Webster, New York. The scanner was used with Scanalyst software from Automatic Identification Systems of Westerville, Ohio.

Frazier Porosity is a measure of air permeability of porous materials and is reported in units of $ft^3/ft^2/min$. Frazier porosity measures the volume of air flow through a material at a differential pressure of 0.5 inches water. An orifice is mounted in a vacuum system to restrict flow of air through the sample to a measurable amount. The size of the orifice depends on the porosity of the material. Frazier porosity is measured using a Sherman W. Frazier Co. dual manometer with calibrated orifice in units of $ft^3/ft^2/min$.

EXAMPLES 1-9

Samples of TYVEK® Type 1082C spunbonded polyethylene sheet with an average basis weight of about 101 g/m^2 (3.0 oz/yd^2) were dipped in a treatment solution containing a surfactant, calcium chloride, colloidal silica and deionized water in the weight percents listed for Examples 1-8 in Table 1. Example 9 is a control sample of the same sheet material that was not treated with the treatment solution. The surfactant was either alcohol ethoxylate propoxylate (MERPOL® LF-H sold by DuPont), polyalkyleneoxide modified heptamethyltrisiloxane (SILWET® L-77 sold by WITCO Corporation of Greenwich, Connecticut), or a combination thereof. A calcium chloride solution formed 5 to 15 weight percent of the treatment solution (from 37.5 weight percent technical grade solution). The positively charged colloidal silica was in the form of a colloidal silica solution (40% solids) (LUDOX® CL-P sold by DuPont).

The wet samples were passed between rubber-coated nip rollers to squeeze out excess solution. Solution pick-up by the sheet was about equal to the weight of the sheet (about 3 ounces on a per square yard basis). The samples were oven dried at 90° to 95° C and then tested for water droplet absorption. The dried sheet samples were ink printed with the seven color blocks described above using the Encad ink jet printer described above. The optical density and color washout was measured on each sample as described above. The percent improvement in optical density was determined by comparing the average optical density (based

on the four primary ink colors) for a treated sample of the example and an untreated control sample (Ex. 9). The dried sample was also printed with a black bar code (using a Hewlett Packard DeskJet 560c printer) and scanned with a bar code scanner, as described above, to determine whether the printed image was clear enough to be read by the bar code scanner. The results are recorded in Table 1 below.

TABLE 1

EXAMPLE	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Treatment Solution									
40% Colloidal Silica Solution (wt. %)	0	0	0	20	20	20	20	20	0
37.5% Calcium Chloride Solution (wt. %)	5	15	5	5	5	5	5	5	0
MERPOL® LF-H (wt. %)	1	1	1	1	2	1	0.5	0.2	0
SILWET® L-77 (wt. %)	0.8	0.8	0.8	0.8	0	0	0	0	0
pH	7.56	7.5	3.36*	4	4	4	4	4	NA
Sheet Properties									
Absorption (microl/mm^2/sec)	1.40	0.99	0.31	0.26	0.44	0.27	0.035	0.008	0.005
Color Washout (%)	8.2	15.7	9.9	9.4	9.3	15.0	6.6	3.5	83.7
Bar Code Readable	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	No
Optical Density - Black	1.07	1.32	1.11	1.25	1.26	1.27	1.35	1.34	0.86
Optical Density - Magenta	0.82	0.95	0.85	0.92	0.93	0.94	1.03	1.07	0.76
Optical Density - Yellow	0.77	0.96	0.80	0.88	0.96	1.01	1.09	1.15	0.87
Optical Density - Cyan	0.70	0.93	0.81	1.01	0.89	1.01	1.11	1.08	0.66
Optical Density - 4 Color Average	0.84	1.04	0.89	1.02	1.01	1.06	1.15	1.16	0.79
Avg. Optical Density Improvement (%) vs. Untreated Sheet - Ex. 9	6	32	13	29	28	34	46	47	NA

** pH adjusted with 18% HCl*

As can be seen from Examples 4-7, a treatment solution of 20% colloidal silica solution (40% solids), 5% calcium chloride solution (37.5% $CaCl_2$), and between 0.5% and 2% surfactant greatly improved the ink jet printability of a spunbonded polyethylene substrate as compared to an untreated sample of the same sheet material (Ex. 9). The treated samples absorbed water

more than 7 times faster than the untreated sample. The untreated sample of Example 9 was five times less waterfast than any of the treated samples of Examples 4-7. Bar codes printed on the treated samples were clear enough to be read by a bar code scanning device, whereas identically printed bar codes on an untreated sample could not be read by a bar code scanner. Finally, the average optical density of the four primary inks printed on the treated samples was between 28% and 46% greater than it was on the untreated control sample.

Examples 1-3 show an alternative embodiment of the invention wherein calcium chloride is the sole source of positively charged species on the printing media. Examples 1 and 2 show that an increase in the weight percent of calcium chloride solution (37.5% $CaCl_2$) improves the optical density of the printed image. Examples 1 and 3 show that reducing the pH of the treatment solution results in only a very modest improvement in optical density when the weight percent of the calcium chloride solution is maintained at a constant 5%. Although Example 2 shows that a significant improvement in optical density can be obtained with calcium chloride as the sole source of positively charged species, the printed image of Example 2 exhibited a relatively high color washout of 15.7%. It was also observed that the printed image of Example 2 was more chalk-like than the images of Examples 4-7. The printed image of Example 2 had less mechanical integrity and was therefore more easily rubbed off than was the case with the printed images of Example 4-7 wherein colloidal silica provided an additional source of positively charged species on the printing media. When calcium chloride is the only source of positively charged species on the printing media, white spots are frequently observed in the printed image where the calcium chloride has become dislodged from the media and taken the printed ink with it.

Without wishing to be bound by theory, it is believed that positively charged colloidal silica forms spheres or clumps that become more mechanically entangled with fibers of the printing media than is the case with the positively charged ions of calcium chloride. Thus, when anionic ink pigments stick to the surface of the spheres of colloidal silica, the printed image has greater mechanical integrity with the fibrous substrate than when calcium chloride is the only source of positively charged species on the printing media. On the other hand, it is believed that the presence of some calcium chloride on the printing media makes the colors in an ink jet printed image appear brighter and clearer because the presence of calcium chloride ions on the surface of the media causes pigment in the anionic inks to flocculate at the surface where the pigments make the greatest contribution to a bright and vivid image.

EXAMPLES 10-16

Samples of TYVEK® Type 1082C sheet, like the sheet used in Examples 1-9, were dipped in a treatment solution containing a surfactant, an acid, and deionized water in the weight percents listed for Examples 10-16 in Table 2. The surfactant was either a potassium butyl phosphate acid ester (ZELAC® -TY sold by DuPont) or octylphenoxypolyethoxyethanol nonionic surfactant (TRITON® X-100 sold by Union Carbide Corporation of Danbury, Connecticut). The acid was either phosphoric acid or a combination of phosphoric acid and citric acid. The treatment solution was prepared by first adding the surfactant to the deionized water and then adjusting the pH by adding small amounts of 80% reagent grade phosphoric acid. In Example 16, where citric acid was also used, the solution was first adjusted to a pH of 1.7 with the phosphoric acid and was then adjusted to a pH of 1.64 with the citric acid. The pH was measured with a Brinmmann, model 691, pH meter.

The wet samples were passed between rubber-coated nip rollers to squeeze out excess solution. Solution pick-up by the sheet was about equal to the weight of the sheet (about 3 ounces on a per square yard basis). The samples were oven dried at 90° to 95° C and then tested for water droplet absorption. The dried sheet samples were ink printed with the seven color blocks described above using the Encad ink jet printer described above. The optical density and color washout was measured on each sample as described above. The percent improvement in optical density was determined by comparing the average optical density (based on the four primary ink colors) for a treated sample of the example and an untreated control sample (Ex. 9). The dried sample was also printed with a black bar code (using a Hewlett Packard DeskJet 560c printer) and scanned with a bar code scanner, as described above, to determine whether the printed image was clear enough to be read by the bar code scanner. The results are recorded in Table 2 below.

TABLE 2

EXAMPLE	**10**	**11**	**12**	**13**	**14**	**15**	**16**
Treatment Solution							
ZELAC® -TY (wt. %)	6.0	6.0	4.0	0	0	0	6.0
TRITON® X-100 (wt. %)	0	0	0	1.0	0.5	0.25	0
Acid	H_3PO_4	H_3PO_4	H_3PO_4	H_3PO_4	H_3PO_4	H_3PO_4	Citric/ H_3PO_4
Solution pH	1.7	2.0	1.7	1.5	1.5	1.5	1.64
Sheet Properties							
Absorption (microl/mm^2/sec)	0.67	0.60	0.07	0.27	0.32	0.14	1.06
Color Washout (%)	3.4	10.5	10.8	7.4	7.0	4.4	6.2
Bar Code Readable	Yes	Yes	No	Yes	Yes	Yes	Yes
Optical Density - Black	1.20	1.10	0.96	0.95	1.05	1.09	1.21
Optical Density - Magenta	0.90	0.90	0.66	0.63	0.77	0.82	0.92
Optical Density - Yellow	0.96	0.93	0.77	0.72	0.80	0.86	0.97
Optical Density - Cyan	0.94	0.92	0.69	0.67	0.76	0.94	0.97
Optical Density - 4 Color Average	1.0	0.96	0.77	0.74	0.85	0.93	1.02
Avg. Optical Density Improvement (%) vs. Untreated Sheet - Ex. 9	27	22	None	None	8	18	29

Examples 10 and 16 demonstrate a solution for treating a fibrous polymeric substrate to make a more ink jet printable media that is comprised of an acid, used in combination with potassium butyl phosphate ester (ZELAC®-TY). Phosphoric acid has been found to be especially effective at improving the ink jet printability of a fibrous substrate, especially when used in combination with citric acid and potassium butyl phosphate ester. Without wishing to be bound by theory, it is believed that the both the phosphoric acid and the acidified potassium butyl phosphate ester serve as positively charged species on the printing media that cause the pigments in anionic ink jet printing inks to flocculate and bind near the surface of the printing media. The acidified potassium butyl phosphate ester has a hydrophobic end that is believed to bind to fibrous substrate of the printing media and a hydrophilic end that is believed to bind to the pigments of an anionic ink jet printing ink. It is further believed that the potassium butyl phosphate ester,

in an acid environment, acts as a wetting agent so as to make the printing media more readily absorb an aqueous ink jet printing ink.

An especially effective treatment solution was prepared by first adding potassium butyl phosphate ester (6% by weight) to deionized water, then adjusting the solution pH to 1.7 by adding small amounts of phosphoric acid to the solution, and then further adjusting the solution pH to 1.64 with the citric acid (Ex. 16). Ink jet printed images printed on the printing media of Example 16 had a more uniform appearance than the images printed on the media of Example 10 wherein the only acid was phosphoric acid. It is believed that the presence of the citric acid results in more spreading of the ink pigments on the surface of the printing media. The fibrous sheet, treated as described in Example 16, absorbed water more than 200 times faster than the untreated sample of Example 9. When tested for waterfastness, the untreated sample of Example 9 lost 13 times more of the color in an ink jet printed image than was lost from the treated sample of Example 16. A bar code printed on the treated sample of Example 16 was clear enough to be read by a bar code scanning device, whereas an identically printed bar code on the untreated sample could not be read by a bar code scanner. In addition, the average optical density of the four primary inks printed on the treated sample of Example 16 was 29% greater than it was on the untreated control sample of Example 9.

Example 11 demonstrates that when the pH of the treatment solution is raised, the potassium butyl phosphate ester (ZELAC®-TY) is a less effective wetting agent such that absorbency of the printing media is reduced and the color washout of an image printed on the media is increased. Example 12 demonstrates that reducing the amount of the potassium butyl phosphate ester in the treatment solution to 4% by weight has a detrimental effect both on the absorbency of the printing media and on the optical density of an image printed on the media. Examples 13-15 demonstrate that use of a nonionic surfactant (TRITON® X-100) in place of the potassium butyl phosphate ester resulted in significantly less improvement in the optical density of an image printed on the treated printing media.

EXAMPLES 17-20

Samples of TYVEK® Type 1082C spunbonded polyethylene sheet with a basis weight of 101 g/m^2 (3.0 oz/yd^2) were dipped in a treatment solution containing positively charged colloidal silica, calcium chloride, aluminum chlorohydrate, aluminum zirconium tetrachlorohydrex glycine, a surfactant, and deionized water. The positively charged colloidal silica solution was the

LUDOX® CL-P (40% solids) used in Examples 4-8, and the calcium chloride was in the from of a 37.5 weight percent technical grade solution. The aluminum chlorohydrate was in the form of a 50 weight percent solution sold as Chlorhydrol®, and the aluminum zirconium tetrachlorohydrex glycine was in the form of a 35% solution sold as REZAL® 36 G, both products of Reheis Inc., Berkeley Heights, NJ. The surfactant was a nonionic alcohol ethoxylate solution with 10% water (TERGITOL® TMN-6 (90% AQ) sold by Union Carbide) at a concentration that was varied in concentration from 0 to 1.5 weight percent. The concentration of the colloidal silica, calcium chloride, aluminum chlorohydrate and aluminum zirconium tetrachlorohydrex glycine was held constant in Examples 17-20. The treatment solution was prepared by first adding the wetting agent to the deionized water while mixing. The remaining ingredents were then gradually added to the water containing the wetting agent while mixing was continued so as to form the treatment solution.

The wet samples were passed between rubber-coated nip rollers to squeeze out excess solution. Solution pick-up by the sheet was about equal to the weight of the sheet (about 3 ounces on a per square yard basis). The samples were oven dried at 90° to 95° C and then tested for water droplet absorption. The dried sheet samples were ink printed with the seven color blocks (described above) using an Encad ink jet printer (described above). The optical density and color washout was measured on each sample as described above. The percent improvement in optical density was determined by comparing the average optical density (based on the four primary ink colors) for a treated sample of the example and an untreated control sample (Ex. 9). The results are recorded in Table 3 below.

TABLE 3

EXAMPLE	17	18	19	20
Treatment Solution				
40% Colloidal Silica Solution (wt. %)	17	17	17	17
37.5% Calcium Chloride Solution (wt. %)	9	9	9	9
REZAL® 36G (wt. %)	3	3	3	3
CHLORHYDROL® (wt.%)	2	2	2	2
TERGITOL® TMN-6 (90%AQ) (wt.%)	1.5	0.5	0.1	0
Sheet Properties				
Absorption (microl/mm^2/sec)	0.45	1.18	0.023	0.022
Color Washout (%)	4.5	2.6	8.2	25.6
Bar Code Readable	Yes	Yes	Yes	Yes
Optical Density - Black	0.98	0.87	1.00	1.01
Optical Density - Magenta	1.20	1.11	1.17	1.20
Optical Density - Yellow	0.99	0.89	0.97	0.96
Optical Density - Cyan	1.39	1.23	1.26	1.33
Optical Density - 4 Color Average	1.14	1.02	1.10	1.12
Avg. Optical Density Improvement (%) vs. Untreated Sheet - Ex. 9	44	29	39	42

Examples 17-20 illustrate another preferred embodiment of the invention. The weight percents of the ingredients in the treatment solutions of Examples 17-20, except for the surfactant, were held constant. Without wishing to be bound by theory, it is believed that the positively charged colloidal silica, the calcium chloride, the aluminum chlorohydrate, and the aluminum zirconium tetrachlorohydrex glycine each serve as a source of positively charged species on the treatment media. As discussed with regard to Examples 4-8 above, it is believed that the positively charged colloidal silica forms spheres or clumps that become mechanically entangled with fibers of the printing media and to which pigment in an anionic ink jet printing ink adhear. The presence of divalent calcium chloride on the printing media makes the colors in an ink jet printed

image appear brighter and clearer. As discussed with regard to Examples 4-8 above, the presence of calcium chloride ions on the surface of the media is believed to make pigment in the anionic inks flocculate near the surface of the media so as to provide a bright and vivid printed image. It is believed that the trivalent aluminum zirconium tetrachlorohydrex glycine and aluminum chlorohydrate compounds of the treatment solution act as strong complexing agents that generate larger pigment flocs than does the calcium chloride so as to improve the mechanical integrity of the ink jet printed image. Treatment of a printing media with the combination of positively charged species of Examples 17-20 makes an ink jet printable media onto which an image with excellent optical density, low color washout, and good rub resistance can be ink jet printed.

Examples 17-20 also demonstrate that absorbency of an ink jet printable media can be improved by increasing the weight percent of the nonionic alcohol ethoxylate surfactant (TERGITOL® TMN-6) in the treatment solution without sacrificing image quality. Examples 17 and 18 show that the presence of 0.5% to 1.5% alcohol ethoxylate surfactant significantly improves the absorbency of the media while the optical density of a printed image is maintained.

EXAMPLES 21-22

In Examples 21 and 22, samples of TYVEK® Type 1070P spun bonded polyethylene sheet material with a basis weight of 71 g/m^2 (2.1 oz/yd^2) that were reinforced with a sheet of CLAF® S1510 cross-laminated reinforcing scrim material with a basis weight of 23 g/m^2 (0.68 oz/yd^2)(sold by Amoco Nisseki CLAF, Inc. of Atlanta, GA) thermally laminated to one side of the TYVEK® sheet were tested as described in Examples 17-20. The sample of Example 21 was dipped in the treatment solution of Example 17 and then oven dried at 90° to 95°C prior to testing. The sample in Example 22 received no treatment prior to testing. The samples were ink printed with the seven color blocks described above using an Encad ink jet printer as described above. The optical density and color washout was measured on each sample as described above. The percent improvement in optical density was determined by comparing the average optical density (based on the four primary ink colors) for the treated sample of Example 21 against the untreated control sample of Example 22. The results are recorded in Table 4 below:

TABLE 4

EXAMPLE	21	22
Treatment Solution		
40% Colloidal Silica Solution (wt. %)	17	0
37.5% Calcium Chloride Solution (wt. %)	9	0
REZAL® 36G (wt. %)	3	0
Chlorohydrol® (wt.%)	2	0
TERGITOL® TMN-6 (90%AQ) (wt.%)	1.5	0
Sheet Properties		
Absorption (microl/mm^2/sec)	0.23	0.005
Color Washout (%)	4.9	78.3
Bar Code Readable	Yes	No
Optical Density - Black	0.95	0.88
Optical Density - Magenta	1.14	0.78
Optical Density - Yellow	0.92	0.77
Optical Density - Cyan	1.27	0.78
Optical Density - 4 Color Average	1.07	0.80
Avg. Optical Density Improvement (%) vs. Untreated Sheet - Ex. 9	34	-

Example 21 demonstrates that a printing media comprised of a sheet of spunbonded polyethylene laminated with a reinforcing scrim material can be made into an excellent ink jet printable media by treating the sheet with a combination of positively charged colloidal silica, calcium chloride, aluminum chlorohydrate, aluminum zirconium tetrachlorohydrex glycine, and a surfactant. It is anticipated that an alternative printing media could be made by thermally laminating sheets of spunbonded sheet material to opposite sides of a sheet of reinforcing scrim material.

EXAMPLES 23-25

Example 23-25 illustrate a number of alternative printing media treatment solutions with non-acid sources of positively charged species. Samples

of TYVEK® Type 1082C spunbonded polyethylene sheet with a basis weight of 101 g/m^2 (3.0 oz/yd^2) were dipped in a treatment solution containing one of the following compound combinations in deionized water:

n-butyl phosphate ester, the oil-in water emulsifier alkoxylate sulfate (TRITON® W-30 sold by Union Carbide) (Ex. 23);

positively charged colloidal silica, a nonionic alcohol ethoxylate surfactant (TERIGITOL® TMN-6 (90%AQ)) and a liquid cationic polydadmac (polydimethyl diallylammonium chloride) coagulant (PERCOL® 406-F from Allied Colloids, Suffolk, VA)(Ex.24);

positively charged colloidal silica, a nonionic alcohol ethoxylate surfactant, and a highly cationic polyacrylamide derivative floculant (C411 from Chemtall, Inc. of Riceboro, Georgia)(Ex. 25).

Concentrations of the ingredients in deionized water are given in Table 5 below. The treatment solution of Example 23 was prepared by first adding the TRITON® W-30 to the deionized water and then adjusting the pH by gradually adding the n-butyl phosphate ester. The solution was continuously mixed using a lab dispersor, model Ultra Turrax T25/S1, manufactured by IKA while adjusting the pH. The treatment solutions in Examples 24 and 25 were prepared by first adding the surfactant and then gradually adding the other ingredients to the solution.

The wet samples were passed between rubber-coated nip rollers to squeeze out excess solution. Solution pick-up by the sheet was about equal to the weight of the sheet (about three ounces on a per square yard basis). The samples were oven dried at 90° to 95°C and then tested for water droplet absorption. The dried sheet samples were ink printed with the seven color blocks (described above) using an Encad ink jet printer (described above). The optical density and color washout was measured on each sample as described above. The percent improvement in optical density was determined by comparing the average optical density (based on the four primary ink colors) for a treated sample of the example and an untreated control sample (Ex. 9). The results are recorded in Table 5 below.

TABLE 5

EXAMPLE	23	24	25
Treatment Solution			
PERCOL® 406-F (wt. %)	-	7	0
C411 (wt. %)	-	0	1
40% Colloidal Silica Solution(wt. %)	-	7	10
TERGITOL® TMN-6 (90%AQ)(wt.%)	-	1.5	1.5
n-butyl phosphate ester (wt. %)	5	-	-
TRITON® W-30 (wt. %)	0.4	-	-
Sheet Properties			
Absorption (microl/mm^2/sec)	1.82	0.13	0.69
Color Washout (%)	6.1	10.3	23.4
Bar Code Readable	Yes	Yes	Yes
Optical Density - Black	0.90	1.11	0.77
Optical Density - Magenta	0.74	1.01	0.72
Optical Density - Yellow	0.78	0.87	0.68
Optical Density - Cyan	0.85	1.03	0.90
Optical Density - 4 Color Average	0.82	1.00	0.77
Avg. Optical Density Improvement (%) vs. Untreated Sheet - Ex. 9	4	27	none

Example 23 shows that a very modest improvement in the optical density of a printed image on a spunbonded polyethylene printing media can be obtained by treating the media with the n-butyl phosphate ester as a source of positively charged species. Example 24 shows that treatment with a cationic polydadmac coagulant (PERCOL® 406-F) yielded some improvement in the optical density of a printed image on a spunbonded polyethylene printing media. No such improvement was found with the cationic polyacrylamide derivative flocculant (C411) of Example 25. The printed images in Examples 23 and 24 were considerably less bright and vivid than ink jet printed images on the more preferred printing media of Examples 4-8, 10, 16 and 17-20.

EXAMPLES 26-28

Samples of a nonwoven spunbonded polypropylene sheet material were treated and evaluated for water droplet absorption, color washout, and optical density of printed color. The polypropylene sheet was made from multi-layered melt spun polypropylene fibers that had been thermally calendered, having a thickness of 229 microns (9 mils), and a basis weight of 126 g/m^2 (3.7 oz/yd^2).

One sample of the sheet material was dipped in Treatment Solution A, one sample of the sheet material was dipped in Treatment Solution B, and a control sample of the sheet material was not treated. Treatment Solution A was the solution containing a surfactant, an acid, and deionized water in the weight percents listed for Example 16 (6% Zelac®-TY; deionized water; pH adjusted to 1.64 with a combination of Phosphoric Acid and Citric Acid). Treatment Solution B was the solution containing colloidal silica, calcium chloride, a surfactant, and deionized water in the weight percents listed for Example 4 (20% Collodial Silica Solution (40% solids); 5% Calcium Chloride Solution (37.5% $CaCl_2$); 1% MERPOL® LF-H; 0.8% SILWET® L-77). Solution pick-up by the sheet was about equal to the basis weight of the sheet. The wet samples were passed between rubber-coated nip rollers to squeeze out excess solution. The samples were oven dried at 90° to 95° C.

Each of the samples was then tested for water droplet absorption as described above. The sheet samples were ink printed with the seven color blocks described above using the Encad ink jet printer described above. The optical density and color washout was measured on each sample as described above. The percent improvement in optical density was determined by comparing the average optical density (based on the four primary ink colors) for the treated sample of the example and the untreated control sample (Ex. 28). The results are recorded in Table 6 below.

TABLE 6

EXAMPLE	26	27	28
Treatment Solution	A	B	Control
Sheet Properties			
Absorption (microl/mm^2/sec)	1.10	0.86	<0.001
Water Washout (%)	12.1	10.0	63.1
Optical Density - Black	1.24	1.25	0.95
Optical Density - Magenta	0.91	0.94	0.76
Optical Density - Yellow	0.99	0.92	0.73
Optical Density - Cyan	0.83	0.89	0.72
Optical Density - 4 Color Average	0.99	1.0	0.79
Avg. Optical Density Improvement (%) vs. Untreated Sheet - Ex. 22	25	27	–

Examples 26-28 show that the ink jet printability of a nonwoven spunbonded polypropylene sheet material is dramatically improved by treatment with either the Treatment Solution A (6% Zelac®-TY; deionized water; pH adjusted to 1.64 with a combination of Phosphoric Acid and Citric Acid) or the Treatment Solution B (20% Collodial Silica Solution (40% solids); 5% Calcium Chloride Solution (37.5% $CaCl_2$); 1% MERPOL® LF-H and 0.8% SILWET® L-77surfactants in deionized water). The physical properties of sheet absorbancy, color washout, and optical density were all improved dramatically by the application of Treatment Solutions A and B to a nonwoven polypropylene sheet material.

EXAMPLES 29-31

Samples of a woven polyester fabric material were treated and evaluated for water droplet absorption, color washout, and optical density of printed color. The polyester fabric was a woven DACRON® polyester, having a thickness of 0.386 mm, and a basis weight of 110 g/m^2 (3.27 oz/yd^2).

One sample of the fabric was dipped in Treatment Solution A, one sample of the fabric was dipped in Treatment Solution B, and a control sample of

the fabric was not treated. Treatment Solution A was the solution containing a surfactant, an acid, and deionized water in the weight percents listed for Example 16 (6% ZELAC® -TY; deionized water; pH adjusted to 1.64 with a combination of Phosphoric Acid and Citric Acid). Treatment Solution B was the solution containing colloidal silica, calcium chloride, a surfactant, and deionized water in the weight percents listed for Example 4 (20% Collodial Silica Solution (40% solids); 5% Calcium Chloride Solution (37.5% $CaCl_2$); 1% MERPOL® LF-H; 0.8% SILWET® L-77). Solution pick-up by the sheet was about equal to the basis weight of the fabric. The wet samples were passed between rubber-coated nip rollers to squeeze out excess solution. The samples were oven dried at 90° to 95° C.

Each of the samples was then tested for water droplet absorption as described above. The sheet samples were ink printed with the seven color blocks described above using the Encad ink jet printer described above. The optical density and color washout was measured on each sample as described above. The percent improvement in optical density was determined by comparing the average optical density (based on the four primary ink colors) for the treated sample of the example and the untreated control sample (Ex. 31). The results are recorded in Table 7 below.

TABLE 7

EXAMPLE	29	30	31
Treatment Solution	A	B	Control
Sheet Properties			
Absorption (microl/mm^2/sec)	*	*	0.004
Water Washout (%)	21.9	37.7	77.2
Optical Density - Black	1.12	1.21	0.70
Optical Density - Magenta	0.82	0.83	0.57
Optical Density - Yellow	0.83	0.82	0.60
Optical Density - Cyan	0.80	0.83	0.55
Optical Density - 4 Color Average	0.89	0.92	0.61
Avg. Optical Density Improvement (%) vs. Untreated Sheet - Ex. 25	46	51	--

**Absorption rate >11 microl/mm^2/sec*

Examples 29-31 show that the ink jet printability of a woven polyester fabric material is dramatically improved by treatment with either the Treatment Solution A (6% Zelac®-TY; deionized water; pH adjusted to 1.64 with a combination of Phosphoric Acid and Citric Acid) or the Treatment Solution B (20% Collodial Silica Solution (40% solids); 5% Calcium Chloride Solution (37.5% $CaCl_2$); 1% MERPOL® LF-H and 0.8% SILWET® L-77 surfactants in deionized water). The physical properties of sheet absorbancy, color washout, and optical density were all improved dramatically by the application of Treatment Solutions A and B to woven polyester fabric.

EXAMPLES 32-34

Samples of a woven cotton fabric material were treated and evaluated for water droplet absorption, color washout, and optical density of printed color. The cottorn fabric was made of 100% woven cotton, and it had a thickness of 0.439 mm, and a basis weight of 137 g/m^2 (4.06 oz/yd^2).

One sample of the fabric was dipped in Treatment Solution A, one sample of the fabric was dipped in Treatment Solution B, and a control sample of the fabric was not treated. Treatment Solution A was the solution containing a surfactant, an acid, and deionized water in the weight percents listed for Example 16 (6% ZELAC® -TY; deionized water; pH adjusted to 1.64 with a combination of Phosphoric Acid and Citric Acid). Treatment Solution B was the solution containing colloidal silica, calcium chloride, a surfactant, and deionized water in the weight percents listed for Example 4 (20% Collodial Silica Solution (40% solids); 5% Calcium Chloride Solution (37.5% $CaCl_2$); 1% MERPOL® LF-H; 0.8% SILWET® L-77). Solution pick-up by the sheet was about equal to the basis weight of the fabric. The wet samples were passed between rubber-coated nip rollers to squeeze out excess solution. The samples were oven dried at 90° to 95° C.

Each of the samples was then tested for water droplet absorption as described above. The sheet samples were ink printed with the seven color blocks described above using the Encad ink jet printer described above. The optical density and color washout was measured on each sample as described above. The percent improvement in optical density was determined by comparing the average optical density (based on the four primary ink colors) for the treated sample of the example and the untreated control sample (Ex. 34). The results are recorded in Table 8 below.

TABLE 8

EXAMPLE	32	33	34
Treatment Solution	A	B	Control
Sheet Properties			
Absorption (microl/mm^2/sec)	*	*	0.003
Color Washout (%)	7.7	9.6	30.4
Optical Density - Black	1.11	1.22	1.04
Optical Density - Magenta	0.78	0.81	0.68
Optical Density - Yellow	0.76	0.83	0.70
Optical Density - Cyan	0.79	0.83	0.72
Optical Density - 4 Color Average	0.86	0.92	0.79
Avg. Optical Density Improvement (%) vs. Untreated Sheet - Ex. 27	9	16	–

**Absorption rate >11 microl/mm^2/sec*

Examples 32-34 show that the ink jet printability of a woven cotton fabric material is improved by treatment with either the Treatment Solution A (6% Zelac-TY; deionized water; pH adjusted to 1.64 with a combination of Phosphoric Acid and Citric Acid) or the Treatment Solution B (20% Collodial Silica Solution (40% solids); 5% Calcium Chloride Solution (37.5% $CaCl_2$); 1% MERPOL® LF-H; 0.8% SILWET® L-77). The physical properties of sheet absorbancy, color washout, and optical density were all improved by the application of Treatment Solutions A and B to woven cotton fabric.

EXAMPLES 35-37

Samples of a woven 50/50 blend of polyester and cotton were treated and evaluated for water droplet absorption, color washout, and optical density of printed color. The fabric blend was made of 50% cotton and 50% polyester. The fabric blend had a thickness of 0.165 mm, and a basis weight of 113 g/m^2 (3.35 oz/yd^2).

One sample of the fabric was dipped in Treatment Solution A, one sample of the fabric was dipped in Treatment Solution B, and a control sample of the fabric was not treated. Treatment Solution A was the solution containing a

surfactant, an acid, and deionized water in the weight percents listed for Example 16 (6% Zelac-TY; deionized water; pH adjusted to 1.64 with a combination of Phosphoric Acid and Citric Acid). Treatment Solution B was the solution containing colloidal silica, calcium chloride, a surfactant, and deionized water in the weight percents listed for Example 4 (20% Collodial Silica Solution (40% solids); 5% Calcium Chloride Solution (37.5% $CaCl_2$); 1% MERPOL® LF-H; 0.8% SILWET® L-77). Solution pick-up by the sheet was about equal to the basis weight of the fabric. The wet samples were passed between rubber-coated nip rollers to squeeze out excess solution. The samples were oven dried at 90° to 95° C.

Each of the samples was then tested for water droplet absorption as described above. The sheet samples were ink printed with the seven color blocks described above using the Encad ink jet printer described above. The optical density and color washout was measured on each sample as described above. The percent improvement in optical density was determined by comparing the average optical density (based on the four primary ink colors) for the treated sample of the example and the untreated control sample (Ex. 37). The results are recorded in Table 9 below.

TABLE 9

EXAMPLE	**35**	**36**	**37**
Treatment Solution	A	B	Control
Sheet Properties			
Absorption (microl/mm^2/sec)	0.031	0.025	0.002
Color Washout (%)	4.1	19.8	24.0
Optical Density - Black	1.07	1.22	0.76
Optical Density - Magenta	0.76	0.81	0.64
Optical Density - Yellow	0.86	0.86	0.67
Optical Density - Cyan	0.80	0.79	0.65
Optical Density - 4 Color Average	0.87	0.92	0.68
Avg. Optical Density Improvement (%) vs. Untreated Sheet - Ex. 31	28	35	--

Examples 35-37 show that the ink jet printability of a woven polyester/cotton blend fabric material is dramatically improved by treatment with either the Treatment Solution A (6% Zelac-TY; deionized water; pH adjusted to 1.64 with a combination of Phosphoric Acid and Citric Acid) or the Treatment Solution B (20% Collodial Silica Solution (40% solids); 5% Calcium Chloride Solution (37.5% $CaCl_2$); 1% MERPOL® LF-H and 0.8% SILWET® L-77 surfactants in deionized water). The physical properties of sheet absorbancy, color washout, and optical density were all improved dramatically by the application of Treatment Solutions A and B to woven polyester/cotton blend fabric.

EXAMPLES 38-62

Examples 38-62 show how the treatment of three different fabrics with various acids improves the ink jet printability of the fabrics. The following fabrics were used:

1. 100% polyester. The polyester fabric was a woven DACRON® polyester, having a thickness of 0.386 mm, and a basis weight of 110 g/m^2 (3.27 oz/yd^2). (hereinafter "Polyester Fabric").

2. 100% Nylon 6,6. The Nylon fabric was a taffetta that had been scoured and desized with a basis weight of 74.5 g/m^2 (2.21 oz/yd^2), and a thickness of 0.132mm (Milliken Style 670922/198) (hereinafter "Nylon Fabric").

3. 70% polyester/30% cotton. The 70/30 polyester/cotton blend fabric was a woven fabric. (hereinafter "Blend Fabric").

The fabrics were dipped in one of the acid solutions listed below. Excess liquids were allowed to drip off and the fabric sheets were dried at 20-40° C. The dried fabrics were taped onto backing paper and printed with the primary inks described above jetted out on a Hewlett Packard DeskJet 560c printer ink jet printer. An untreated control sample of each of the three fabrics was also printed. The seven color square pattern used for measuring optical density, as described above, were printed on the sample. In addition, a print pattern that included an array of colored lines on a yellow background was printed for the purpose of making a visual comparison of line acuity and image resolution.

The optical density was measured on each sample as described above. The percent improvement in optical density was determined by comparing the average optical density (based on the four primary ink colors) for a treated sample of the example and an untreated control sample.

Dot spread control was evaluated visually. Uncontrolled ink spread leads to "wicking" or "bleed" effects where an ink color migrates into adjacent unprinted areas. Often, such "wicking" or "bleed" occurs along the fibers of a sheet or fabric. Uncontrolled dot spread results in lines with edges that appear fuzzy and have poor definition between colored areas. A dot spread control rating of *Poor* ("P") represents a print exhibiting little definition of boundary between one color and an adjacent color or unprinted area. A dot spread control rating of *Fair* ("F") represents a print exhibiting clear definition of boundary between one color and an adjacent color or unprinted area, but still representing color migration between one color and an adjacent color. A dot spread control rating of *Good* ("G") represents a print exhibiting clear, sharp definition of boundary between one color and an adjacent color or unprinted area.

The results for the Polyester Fabric samples are recorded in Table 10 below. The results for the Nylon Fabric samples are recorded in Table 11 below. The results for the Blend Fabric samples are recorded in Table 12 below.

Acid Solutions

Treatment Solution No.	Acid Concentration in Water	Solution pH
C	10% succinic	2.14
D	10% sulfamic (amidosulfonic)	0.04
E	14% oxalic	0.54
F	20% citric	1.56
G	20% maleic	0.84
H	20% malic	1.64
I	20% methoxyacetic	1.61
J	20% phosphoric	0.91
K	sulfanilic at saturation (~ 2%) (o-aminobenzene sulfonic)	2.09
L	tetra-boric at saturation (~ 5%)	2.25
M	valeric at saturation (~ 3%) (pentanoic)	2.69
N	10% citric	1.70
O	50% citric	1.36
P	3% hydrochloric	0.04
Q	3% hydrochloric, 5% ZELEC-TY	0.04
R	0.3% benzoic	2.90
S	0.1% caprylic	3.74

TABLE 10 (Polyester Fabric)

EXAMPLE	38	39	40	41	42	43
Treatment Solution	F	J	E	D	H	Control
pH	1.56	0.91	0.54	0.04	1.64	
Sheet Properties						
Optical Density - Black	1.16	1.15	0.96	1.09	1.15	0.80
Optical Density - Magenta	0.74	0.79	0.70	0.70	0.75	0.57
Optical Density - Yellow	0.80	0.83	0.74	0.76	0.77	0.59
Optical Density - Cyan	0.79	0.82	0.76	0.80	0.80	0.61
Optical Density - 4 Color Average	0.87	0.90	0.79	0.84	0.87	0.64
Avg. Optical Density Improvement (%) vs. Untreated Sheet - Ex. 37	36	41	23	31	36	–
Dot Spread Control Rating	G	G	G	G	G	F

TABLE 11 (Nylon Fabric)

EXAMPLE	44	45	46	47	48	49	50
Treatment Solution	L	M	C	G	I	K	N
pH	2.25	2.69	2.14	0.84	1.61	2.09	1.70
Sheet Properties							
Optical Density - Black	0.92	0.96	1.15	1.11	1.02	0.98	1.16
Optical Density - Magenta	0.67	0.71	0.76	0.74	0.70	0.72	0.76
Optical Density - Yellow	0.64	0.60	0.79	0.79	0.64	0.67	0.71
Optical Density - Cyan	0.69	0.74	0.81	0.80	0.76	0.79	0.83
Optical Density - 4 Color Average	0.73	0.75	0.88	0.86	0.78	0.79	0.87
Avg. Optical Density Improvement (%) vs. Untreated Sheet - Ex. 50	9	12	31	28	16	18	30
Dot Spread Control Rating	P	P	G	G	G	G	G

TABLE 11 (Nylon Fabric)
(continued)

EXAMPLE	51	52	53	54	55	56
Treatment Solution	O	P	Q	R	S	Control
pH	1.36	0.04	0.04	2.90	3.74	
Sheet Properties						
Optical Density - Black	1.21	1.11	1.19	0.84	1.01	0.87
Optical Density - Magenta	0.76	0.74	0.84	0.66	0.66	0.56
Optical Density - Yellow	0.75	0.72	0.85	0.60	0.58	0.61
Optical Density - Cyan	0.85	0.78	0.85	0.75	0.67	0.64
Optical Density - 4 Color Average	0.89	0.84	0.93	0.71	0.73	0.67
Avg. Optical Density Improvement (%) vs. Untreated Sheet - Ex. 50	33	25	39	6	9	–
Dot Spread Control Rating	G	G	G	P	P	P

TABLE 12 (Blend)

EXAMPLE	57	58	59	60	61	62
Fabric	Blend	Blend	Blend	Blend	Blend	Blend
Treatment Solution	F	J	E	D	H	Control
pH	1.56	0.91	0.54	0.04	1.64	–
Sheet Properties						
Optical Density - Black	1.26	1.22	1.05	1.06	1.27	0.88
Optical Density - Magenta	0.81	0.76	0.69	0.71	0.82	0.58
Optical Density - Yellow	0.85	0.82	0.71	0.73	0.85	0.58
Optical Density - Cyan	0.88	0.89	0.77	0.75	0.89	0.63
Optical Density - 4 Color Average	0.95	0.92	0.81	0.81	0.96	0.67
Avg. Optical Density Improvement (%) vs. Untreated Sheet - Ex. 56	42	37	21	21	43	–
Dot Spread Control Rating	G	G	G	G	G	G

It will be apparent to those skilled in the art that modifications and variations can be made in printing media of this invention. The invention in its broader aspects is, therefore, not limited to the specific details or the illustrative examples described above. Thus, it is intended that all matter contained in the foregoing description and examples shall be interpreted as illustrative and not in a limiting sense.

WHAT IS CLAIMED IS:

1. An ink jet printable media comprising:

a fibrous polymeric substrate having positively charged species on the surface thereof;

said ink jet printable media having

a unitary structure,

a tensile strength of at least 20 N/2.54 cm,

a basis weight of less than 8 oz/yd^2,

a water absorption rate, according to TAPPI T558 pm-95, of at least 0.01 microl/mm^2/sec, and

a color washout, when printed with an ink jet ink according to the IJE method, of less than 50%.

2. The ink jet printable media according to claim 1, wherein said ink jet printable media has a color washout, according to the IJE method, of less than 25%, and a water absorption rate, according to TAPPI T558 pm-95, of at least 0.2 microl/mm^2/sec.

3. The ink jet printable media according to claim 1, wherein said fibrous polymeric substrate is a nonwoven sheet.

4. The ink jet printable media according to claim 3, wherein

said nonwoven sheet is a spunbonded polyolefin sheet,

an ink jet printed bar code printed on the media using a black pigment-based ink is readable by a bar code scanner when tested according to ANSI X3.182-1990, and

the media has a four color optical density, measured according to the OD method, of at least 0.85.

5. The ink jet printable media according to claim 2, wherein said fibrous substrate is comprised of fibers having positively charged colloidal silica and a wetting agent on the surface of said fibers.

6. The ink jet printable media according to claim 5, wherein said fibrous substrate is comprised of fibers having calcium chloride on the surface of said fibers.

7. The ink jet printable media according to claim 2, wherein said fibrous substrate is comprised of fibers having a wetting and at least one compound selected from the group of water soluble compounds of calcium, aluminum, magnesium and zirconium on the surface of said fibers.

8. The ink jet printable media according to claim 2, wherein said fibrous substrate is comprised of fibers having positively charged protons and a wetting agent on the surface of said fibers.

9. A composite sheet comprised of the ink jet printable media of claim 1 laminated to a reinforcing scrim material.

10. An ink jet printable media comprising:

a unitary sheet of polymer fibers having positively charged colloidal silica and a wetting agent on the surface of the fibers of the sheet;

said ink jet printable media having

a tensile strength of at least 20 N/2.54 cm,

a basis weight of less than 8 oz/yd^2,

a water absorption rate, according to TAPPI T558 pm-95, of at least 0.01 microl/mm^2/sec, and

a color washout, according to the IJE method, of less than 50%.

11. The ink jet printable media according to claim 10, wherein the fibers of said fibrous substrate have calcium chloride, aluminum chlorohydrate, and aluminum zirconium tetrachlorohydrex glycine on the surface thereof.

12. The ink jet printable media according to claim 10, wherein the polymer fibers comprise flash-spun polyolefin fibers.

13. An ink/printing media set comprising:

(a) an ink containing an aqueous carrier medium and a dye or pigment colorant; and

(b) an ink jet printable media comprising a fibrous polymeric substrate having positively charged species on the surface thereof, wherein the media has a unitary structure, a tensile strength of at least 20 N/2.54 cm, a basis weight of less than 8 oz/yd^2, a water absorption rate, according to TAPPI T558 pm-95, of at least 0.01 microl/mm^2/sec, and a color washout, according to the IJE method, of less than 50%.

14. The ink/printing media set of claim 13 wherein said ink comprises an anionic pigment colorant dispersed in an aqueous carrier medium.

15. The ink/printing media set of claim 14 wherein said ink jet printable media has a color washout, according to the IJE method, of less than 25%, and a water absorption rate, according to TAPPI T558 pm-95, of at least 0.25 microl/mm^2/sec.

16. The ink/printing media set of claim 15 wherein said fibrous polymeric substrate is comprised of fibers having positively charged colloidal silica and a wetting agent on the surface of said fibers.

17. The ink/printing media set of claim 15 wherein said fibrous polymeric substrate is comprised of fibers having positively charged protons and a wetting agent on the surface of said fibers.

18. A process for making an ink jet printable media comprising the steps of:

forming a solution comprising water, and a source of positively charged species;

wetting a fibrous polymeric substrate with said solution, said substrate having a tensile strength of at least 20 N/2.54 cm and a basis weight of less than 8 oz/yd^2; and

drying said substrate, said dried substrate having a water absorption rate, according to TAPPI T558 pm-95, of at least 0.01 microl/mm^2/sec, and a color washout, according to the IJE method, of less than 50%.

19. The process of claim 18 wherein said source of positively charged species is selected from the group of positively charged colloids, acids, and water soluble compounds of calcium, aluminum, magnesium and zirconium.

20. The process of claim 19 wherein said dried fibrous polymeric substrate has a four color optical density, measured according to the OD method, that is at least 8% greater than the four color optical density of the fibrous polymeric substrate before the substrate is wetted with said solution.

21. The process of claim 19 wherein said solution includes an acid and wherein the pH of the solution is less than 2.5.

22. The process of claim 21 wherein said solution is comprised of between 2% and 10% by weight of a potassium butyl phosphate ester and wherein said acid includes phosphoric acid.

23. The process of claim 19 wherein said solution is comprised of at least 2% by weight colloidal silica, and at least 0.4% by weight of a surfactant.

24. The process of claim 23 wherein said surfactant is selected from the group of alcohol ethoxylate, alcohol ethoxylate propoxylate, and polyalkyleneoxide modified heptamethyltrisiloxane.

25. The process of claim 23 wherein said solution is comprised of between 4% and 12% by weight of colloidal silica, between 0.4% and 5% by weight of surfactant, and between 1% and 10% calcium chloride.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/27342

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B41M5/00 D06P5/00 D04H3/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B41M D06P D04H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 95, no. 6, 31 July 1995 & JP 07 068922 A (MITSUBISHI PAPER MILLS, LIMITED), 14 March 1995 see abstract	1-25
A	PATENT ABSTRACTS OF JAPAN vol. 98, no. 2, 30 January 1998 & JP 09 267549 A (CANON INCORPORATED), 14 October 1997 see abstract	1-25
A	US 4 636 409 A (R.ARAI ET AL.) 13 January 1987 see claims 1,5,7,12-17; figure 4 see column 4, line 21 - line 51 see column 5, line 34 - line 54 see example 1	1-25

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search	Date of mailing of the international search report
2 March 1999	15/03/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Bacon, A

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 709 222 A (CANON KABUSHIKI KAISHA) 1 May 1996 see claims 1-3; examples 13-24 see page 9, line 5 - line 9	1-25
A	EP 0 771 670 A (IRIS GRAPHICS, INC.) 7 May 1997 see page 2, line 29 - line 34; claims 1-4 see page 3, line 14 - line 50; examples 1-3	1-25

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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